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Novel Approaches to the Sampling of Atmospheric Aerosols and Determination of Chemical Composition

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Academic Dissertation

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CONTENT

PREFACE

This thesis is based on experimental work carried out in the Laboratory of Analytical Chemistry of the Department of Chemistry, University of Helsinki, during the years 2007-2011. Funding for the work was provided by the Academy of Finland, the Emil Aaltonen Foundation, the Walter and Lisi Wahls Foundation, and the University of Helsinki.

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Above all, loving thanks to my parents, Irina and Aleksandr, and all my friends for their support.

ABSTRACT

The Earth's climate is a highly dynamic and complex system in which atmospheric aerosols have been increasingly recognized to play a key role. Aerosol particles affect the climate through a multitude of processes, directly by absorbing and reflecting radiation and indirectly by changing the properties of clouds. Because of the complexity, quantification of the effects of aerosols continues to be a highly uncertain science. Better understanding of the effects of aerosols requires more information on aerosol chemistry.

Before the determination of aerosol chemical composition by the various available analytical techniques, aerosol particles must be reliably sampled and prepared. Indeed, sampling is one of the most challenging steps in aerosol studies, since all available sampling techniques harbor drawbacks. In this study, novel methodologies were developed for sampling and determination of the chemical composition of atmospheric aerosols. In the particle-into-liquid sampler (PILS), aerosol particles grow in saturated water vapor with further impaction and dissolution in liquid water. Once in water, the aerosol sample can then be transported and analyzed by various off-line or on-line techniques. In this study, PILS was modified and the sampling procedure was optimized to obtain less altered aerosol samples with good time resolution. A combination of denuders with different coatings was tested to adsorb gas phase compounds before PILS. Mixtures of water with alcohols were introduced to increase the solubility of aerosols. Minimum sampling time required was determined by collecting samples off-line every hour and proceeding with liquid-liquid extraction (LLE) and analysis by gas chromatography-mass spectrometry (GC-MS).

The laboriousness of LLE followed by GC-MS analysis next prompted an evaluation of solid-phase extraction (SPE) for the extraction of aldehydes and acids in aerosol samples. These two compound groups are thought to be key for aerosol growth. Octadecylsilica, hydrophilic-lipophilic balance (HLB), and mixed phase anion exchange (MAX) were tested as extraction materials. MAX proved to be efficient for acids, but no tested material offered sufficient adsorption for aldehydes. Thus, PILS samples were extracted only with MAX to guarantee good results for organic acids determined by liquid chromatography-mass spectrometry (HPLC-MS).

On-line coupling of SPE with HPLC-MS is relatively easy, and here on-line coupling of PILS with HPLC-MS through the SPE trap produced some interesting data on relevant acids in atmospheric aerosol samples.

A completely different approach to aerosol sampling, namely, differential mobility analyzer (DMA)-assisted filter sampling, was employed in this study to provide information about the size dependent chemical composition of aerosols and understanding of the processes driving aerosol growth from nano-size clusters to climatically relevant particles (>40 nm). The DMA was set to sample particles with diameters of 50, 40, and 30 nm and aerosols were collected on teflon or quartz fiber filters. To clarify the gas-phase contribution, zero gas-phase samples were collected by switching off the DMA every other 15 minutes. Gas-phase compounds were adsorbed equally well on both types of filter, and were found to contribute significantly to the total compound mass. Gas-phase adsorption is especially significant during the collection of nanometer-size aerosols and needs always to be taken into account.

Other aims of this study were to determine the oxidation products of β-caryophyllene (the major sesquiterpene in boreal forest) in aerosol particles. Since reference compounds are needed for verification of the accuracy of analytical measurements, three oxidation products of β-caryophyllene were synthesized: β-caryophyllene aldehyde, β-nocaryophyllene aldehyde, and β-caryophyllinic acid. All three were identified for the first time in ambient aerosol samples, at relatively high concentrations, and their contribution to the aerosol mass (and probably growth) was concluded to be significant.

Methodological and instrumental developments presented in this work enable fuller understanding of the processes behind biogenic aerosol formation and provide new tools for more precise determination of biosphere-atmosphere interactions.

ABBREVIATIONS

AMS	aerosol mass spectrometer
APCI	atmospheric pressure chemical ionization
APPI	atmospheric pressure photoionization
ASE	accelerated solvent extraction
C18	octadecyl silica
CCN	cloud condensation nuclei
DMA	differential mobility analyzer
DMPS	differential mobility particle sizer
DSAE	dynamic sonication-assisted extraction
EI	electron impact ionization
ESI	electrospray ionization
FID	flame ionization detector
GC-MS	gas chromatography-mass spectrometry/gas chromatograph-mass spectrometer
HEPA	high efficiency particulate filter
HGA	3-hydroxyglutaric acid
HLB	hydrophilic-lipophilic balance
HPLC-MS	high performance liquid chromatography-mass spectrometry/high performance liquid chromatograph-mass spectrometer
HVS	high volume sampler
IC	ion chromatography
I.D.	inner diameter
IPCC	Intergovernmental Panel on Climate Change
IS	internal standard
ITMS	ion trap mass spectrometer
LC-MS	liquid chromatography-mass spectrometry/ liquid chromatograph-mass spectrometer
LLE	liquid-liquid extraction

MAX	mixed phase anion exchange material
NMR	nuclear magnetic resonance spectroscopy
PAH/PAHs	polycyclic aromatic hydrocarbon/ polycyclic aromatic hydrocarbons
PEEK	poly(etheretherketone)
PHWE	pressurized hot water extraction
PILS	particle-into-liquid sampler
PM10	particulate matter in aerodynamic diameter less than 10 µm
PM2.5	particulate matter in aerodynamic diameter less than 2.5 µm
SAE	sonication-assisted extraction
SAX	strong anion exchange material
SFE	supercritical fluid extraction
SLE	solid-liquid extraction
SMEAR	Station for Measuring Forest Ecosystem Atmosphere Relations
SOA	secondary organic aerosol
SPE	solid-phase extraction
TLC	thin layer chromatography
TOC	total organic carbon
ToF-MS	time-of-flight mass spectrometry/ time-of-flight mass spectrometer
TSP	total suspended particles
UV	ultraviolet light

SYMBOLS

C	slip correction factor
d_p	particle diameter, nm
Qs	aerosol flow, L/min
Qsh	sheath air flow, L/min
Stk	Stokes number
U	jet velocity, m/s
V	voltage, V
W	nozzle diameter, mm
η	air viscosity, kg/(m*s)
ρ_p	particle density, g/cm^3

LIST OF ORIGINAL PAPERS

This thesis is based on the following papers, hereafter referred to by their Roman numerals [I-V]:

I **Parshintsev, J.**, Räsänen, R., Hartonen, K., Kulmala, M., Riekkola, M.-L. (2009) Analysis of organic compounds in ambient aerosols collected with the particle-into-liquid sampler, Boreal Environ. Res. 14, 630-640, Copyright Boreal Environment Research Publishing Board 2009

II **Parshintsev, J.,** Hyötyläinen, T., Hartonen, K., Kulmala, M., Riekkola, M.-L. (2010) Solid phase extraction of organic compounds in atmospheric aerosol particles collected with the particle-into-liquid sampler and analysis by liquid chromatography-mass spectrometry, Talanta 80, 1170-1176, Copyright Elsevier B.V. 2010

III **Parshintsev, J.,** Kivilompolo, M., Ruiz-Jimenez, J., Hartonen, K., Kulmala, M., Riekkola, M.-L. (2010) Particle-into-liquid sampler on-line coupled with solid-phase extraction-liquid chromatography-mass spectrometry for the determination of organic acids in atmospheric aerosols, J. Chromatogr. A 1217, 5427-5433, Copyright Elsevier B.V. 2010

IV **Parshintsev, J.,** Ruiz-Jimenez, J., Petäjä, T., Hartonen, K., Kulmala, M., Riekkola, M.-L. (2011) Comparison of quartz and teflon filters for simultaneous collection of size-separated ultrafine aerosol particles and gas-phase zero samples, Anal. Bioanal. Chem. in print. Copyright Springer-Verlag 2011, doi: 10.1007/s00216-011-5041-0

V **Parshintsev, J.,** Nurmi, J., Kilpeläinen, I., Hartonen, K., Kulmala, M., Riekkola, M.-L. (2008) Preparation of β-caryophyllene oxidation products and their determination in ambient aerosol samples. Anal. Bioanal. Chem. 390, 913-919, Copyright Springer-Verlag 2008

I took the main responsibility for the planning, the experimental work, data evaluation, and writing of papers **I-III** and **V**. In paper **IV** I was responsible for the planning, data evaluation, writing of the paper and for part of the experimental work.

1 INTRODUCTION

Atmospheric aerosol particles have become a topic of keen interest for researchers in the field of climate change. The main reason for this interest is the ability of these particles to affect climate through direct and indirect processes, including absorbing and reflecting radiation and changing the properties of clouds. Aerosols are highly complex, since their size dependent chemical composition differs in time and space. Because of the complexity, quantification of the climate effects of aerosols continues to be highly uncertain and a challenge to researchers [Pöschl et al. 2005, Ayash et al. 2009].

Over half of the submicron aerosol mass in the troposphere consists of organic material, especially oxygenated compounds [Zhang et al. 2007, Jimenez et al. 2009]. Highly oxidized compounds, such as carboxylic acids and keto- and dicarboxylic acids, are of greatest interest because of their low saturation pressure and consequent high aerosol forming potential. Gas-phase oxidation products with sufficiently low vapor pressure can form secondary organic aerosols (SOA) by condensing/partitioning on pre-existing particles, or they can undergo nucleation to form new particles [Hoffmann et al. 1997]. It is widely recognized that acids formed by the oxidation of terpenes play a major role in biogenic SOA formation because of their abundance in the atmosphere and low vapor pressure. In view of their importance, the acids formed from oxidation of terpenes in ambient aerosol particles have attracted special attention [Jang et al. 2002, Anttila et al. 2005, Warnke et al. 2006, Szmigielski et al. 2007].

The collection of aerosol particles is one of the most difficult steps in the analytical procedure. Atmospheric aerosols are usually collected on a filter or an impactor plate and analyzed either off-line by one of various techniques or directly with an aerosol mass spectrometer [Jimenez et al. 2003, Drewnick et al. 2005, Canagaratna et al. 2007]. The particle-into-liquid sampler (PILS), announced by Weber et al. in 2001, is recognized as a useful device for the collection of aerosols with diameters less than 10 µm (PM10) or less than 2.5 µm (PM2.5). Recently it has been modified for ground and airborne measurements of water-soluble aerosol composition [Orsini et al. 2003]. The PILS combines two conventional techniques in aerosol measurements: particle growth in supersaturated water vapor and impaction of the particles on a quartz plate. In the past, the device has mostly been used for the determination of ion composition of atmospheric aerosols by on-line coupling with ion chromatographs [Weber et al. 2001, Orsini et al. 2003] and

for the determination of water-soluble organic carbon [Sullivan et al. 2004]. In theory, less abundant species in PILS samples can be determined off-line by conventional chromatographic techniques. Since continuous sample flows can be pretreated and analyzed on-line, PILS could also be a useful technique for the determination of real-time atmospheric aerosol chemical composition.

The growth of atmospheric aerosols to climatically relevant particles occurs in size range from a few to 100 nanometers, which means that sample collection for studies clarifying aerosol growth must be done with devices offering specific size selection. Determination of the chemical composition of these small particles is critical if we are to understand what compounds are participating in this globally important process. Differential mobility analyzers (DMA) offer an answer and have already been applied for the collection of nanometer sized aerosols in narrow size distributions [Laitinen et al. 2010]. Unfortunately, since the mass of organic carbon in samples collected with the help of DMA is but a few micrograms, simultaneous gas-phase adsorption constitutes a major drawback of the technique. For reliable sampling, the effect of gas-phase adsorption/partitioning on the results needs to be known for the most common filter types, teflon and quartz.

The research presented here was focused on the development of sampling techniques for the more selective collection of aerosol particles and on the development of analysis techniques, both on-line coupled with sampling and sample treatment and off-line. To make the determination of important products of oxidation of terpenes more accurate, several compounds were synthesized and characterized (**Papers II, V**). The particle-into-liquid sampler was optimized for the collection of atmospheric aerosol samples in order to analyze off-line the oxidation products of α-pinene (**Paper I**). Solid-phase extraction (SPE) was utilized in the treatment of PILS samples for HPLC-MS and GC-MS analyses (**Paper II**). To minimize the amount of labor and errors of methods, PILS was also coupled on-line with HPLC-MS through an SPE trap (**Paper III**). A novel setup for simultaneous zero (gas-phase) sample collection was presented and used for the correction of DMA-assisted sampling (**Paper IV**).

2 AIMS OF THE STUDY

General aims

The overall aim of the study was to develop tools for the clarification of the chemistry involved in biogenic aerosol formation and growth, so allowing more precise determination of biosphere-atmosphere interactions. An overview of the study is presented in **Figure 1**.

Targeted aims of the research were

- to improve existing sampling techniques and to develop new ones for specific instrumental analytical techniques (Papers **I,II,IV**)

- to determine the unwanted alterations in the chemical composition of aerosol samples during filter sampling and to develop tools for their minimization (**III, IV**)

- to determine the contribution of gas-phase compounds to measured amounts of compounds (**IV**)

- to synthesize reference compounds for verification of the accurate determination of oxidized terpenes and the contribution of these terpenes to the chemical composition and life cycle of biogenic atmospheric aerosols (**II, V**)

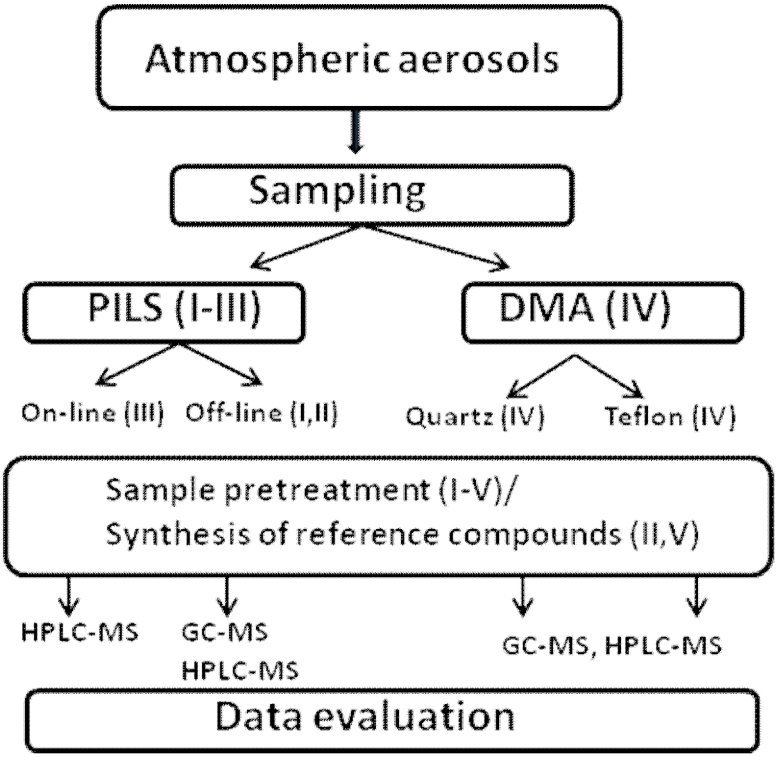

Figure 1. Overview of the study. Roman numerals in brackets refer to the publications of the thesis.

3 ATMOSPHERIC AEROSOLS

Aerosols are defined as a suspension of solid or liquid particles in a gas. The size of atmospheric aerosols varies widely, from a few nanometers (nucleation mode) to a few hundred micrometers (coarse particles, dust). Atmospheric aerosol particles are of primary origin when they are emitted directly (volcanic eruptions, sea salt, soot) and of secondary origin when gas-phase compounds react in the atmosphere to form less volatile compounds [Seinfeld and Pandis 1998]. In addition, aerosols can be classified as anthropogenic (direct traffic emissions) and biogenic (bacteria, fungi [Elbert et al. 2007] but mostly secondary organic aerosols, SOA). Biogenic aerosols have been under extensive study during recent decades.

The most interesting property of atmospheric aerosols is their tendency to grow in size. Figure 2 presents a typical aerosol growth episode, called an "event". The process starts with the emission of organic gas-phase compounds, for example, by trees. Later, if atmospheric conditions are right (warm calm weather, presence of UV light), the compounds may be oxidized in reactions with low troposphere ozone, nitrogen oxides, hydroxyl radicals, etc. A typical example is oxidation of α-pinene emitted by coniferous trees to form pinic and *cis*-pinonic acid [O'Dowd et al. 2002]. Another example is the oligomerization of volatile species such as methylglyoxal [DeHaan et al. 2011]. These low volatility compounds are present in ambient aerosols of different sizes, which means that one path for particle growth in the atmosphere is the adsorption/partitioning of low volatile species on pre-existing particles. The original small particles may be formed by homogeneous or heterogeneous nucleation of oxidized organic vapors with water, sulfuric acid, or ammonia [Winkler et al. 2008, Gaman et al. 2004, Kulmala et al. 2004, Sipilä et al. 2010].

Once particles achieve sizes over 40 nm, they can act as cloud condensation nuclei (CCN) [Cruz et al. 1997] and start to affect the climate directly by absorbing and reflecting radiation, and also indirectly by changing the properties of clouds. As a consequence, the Earth's atmosphere beneath the clouds is cooled [Charlson et al. 1992]. This cooling effect of atmospheric aerosols is of great significance since, during the last century, the Earth's surface temperature has increased by 0.74 °C, reaching the highest level in the last millennium (IPCC 2007). The research on biosphere-atmosphere interactions through aerosol chemistry and physics has assumed a high level of importance because of the globally important consequences. In particular, determination

of atmospheric aerosol chemical composition is essential to understand the contribution of biogenic gas-phase compounds. This new knowledge will help us to determine the effects of the biosphere on climate and to estimate these effects for the future climate.

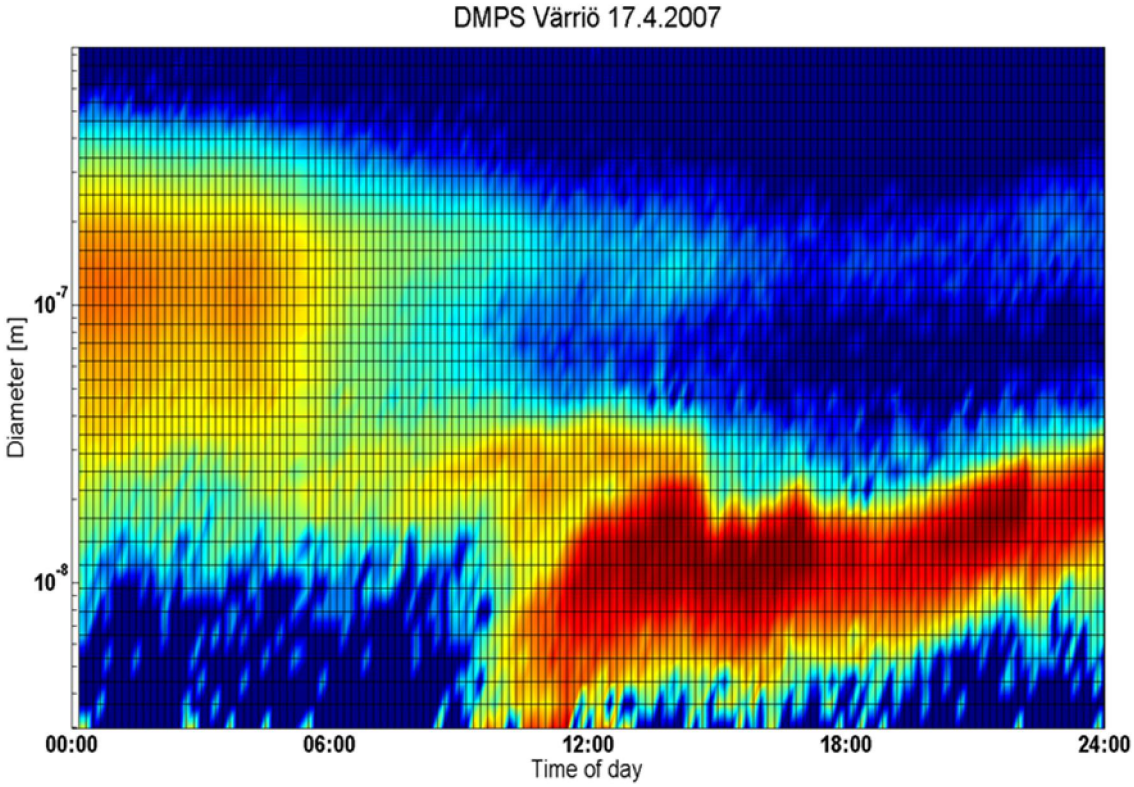

Figure 2. New particle formation event observed at SMEAR I station on 17 April, 2007 with use of a differential mobility particle sizer (DMPS).

Sampling is almost always the most challenging step of the analytical cycle. This is particularly true for atmospheric aerosols, whose chemical composition varies widely in size, time, and space.

3.1 Sampling techniques for atmospheric aerosols

Sampling techniques for atmospheric aerosols can usefully be divided into four groups according to the type of sampling (on-line or off-line) and the size of the sampled aerosols (total suspended particles or size separated fraction). The most common techniques are off-line sampling with size separation (PM10, PM2.5) since these are easy to apply and accepted by environmental protection authorities [Directive 2008/50/EC]. Aerosols with sizes PM10 or PM2.5 are collected on filters or impactor plates by cyclone and impactor. Impactors are the more popular since particles of different aerodynamic sizes can be collected simultaneously; cyclones separate just one size at a time. Figure 3 shows a schematic representation of the working principle of an impactor.

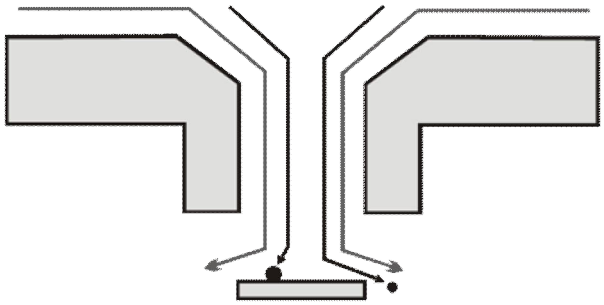

Figure 3. Schematic representation of the working principle of an impactor.

$$Stk = \frac{\rho_p C d_p^2 U}{9\eta W} \quad (1)$$

The working principle of the impactor can be explained by equation 1, which presents the calculation of Stokes number (Stk). In the equation ρ_p is particle density, C the slip correction factor, d_p particle diameter, U jet velocity, η air viscosity, and W nozzle diameter. If Stk is close to zero (Stk « 1) the particle will follow the streamlines of the flow and if it is » 1 the particle

will collide with the impacting plate because of inertia. This equation is used to calculate the cut-size of the impactor stage. Usually, there are many stages in an impactor device, which allows simultaneous collection of samples with different particle sizes, an especially important feature if changes in composition according to size are of interest.

Impactors have been successfully used in many studies. For instance, the particle size distribution of main anions (oxalate, formate, acetate) in eastern Mediterranean aerosols was determined with a Berner-type impactor [Bardouki et al. 2003], and the particle size distribution of 25 elements and 13 ions in the Helsinki area was determined with virtual and Berner-type impactors [Pakkanen et al. 2001].

As noted above, cyclones are used for the separation of particles of one particular size (classification by the time of flight). A scheme of the working principle of the cyclone is shown in Figure 4. Briefly, if the sample air-flow rate remains constant, then centrifugal, gravitational, and inertial principles will cause the particles of a calculated cut-off diameter to spiral downward and out of the flow stream and drop into a dust collection cavity, which can be coated with vacuum grease. Particles of smaller diameter reverse direction and spiral upwards near the cyclone axis to an exit tube. Particles exiting the cyclone can be collected on a filter.

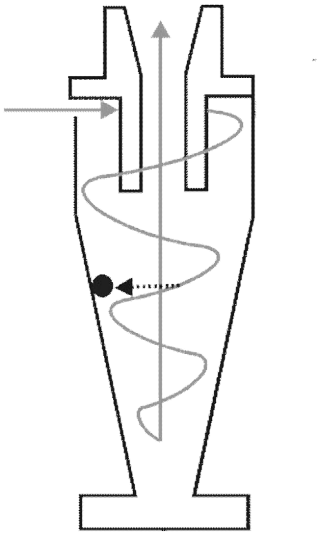

Figure 4. The principle of particle size separation in a cyclone.

Like impactors, cyclones are widely used. For example, PM2.5 samples were collected with a cyclone and teflon filters to study the chemical composition of aerosols in Vermont [Polissar et al. 2001]. In another study, an air sample containing size separated aerosols from a cyclone was divided into several fractions, which were filtered in different ways to get samples for the analysis of major cations, anions, elemental and organic carbon, total mass, and trace elements [Christoforou et al. 2000].

A popular way to sample atmospheric aerosols without size separation is high volume sampling (HVS). In this technique aerosols are typically collected onto quartz fiber filters at relatively high flow rates (tens of cubic meters per hour) [Ho et al. 2003]. Bioaerosols have also been collected directly onto agar plate [An et al. 2004]. Use of HVS is justified where the concentration of aerosols is too low for size separated sampling (clean rural sites) and size dependent composition is not of great importance. To use HVS at low flow rates would translate into such long sampling times that the sample might be affected. Shimmo et al. [2004] carried out an overall chemical characterization of aerosol particles in Finnish boreal forest by analyzing quartz filter samples (240 mm diameter) collected by HVS at 80-90 m^3h^{-1}. They also determined the concentrations of polycyclic aromatic hydrocarbons (PAH) in Helsinki city area aerosols from filters (glass fiber, 25 cm*20 cm) after collection by HSV at flow rate of 100 m^3h^{-1} [Shimmo et al. 2002].

Cyclones and impactors have many disadvantages, the main one being the long sampling time needed to obtain sufficient mass for the analysis. The same problem afflicts HVS, even though sampling time is much shorter, since the amount of air passing through the filter is very high. With long sampling times or high air flow, various processes can take place on the filters. Adsorption of gas-phase compounds, especially on quartz filters, is a particularly well-known problem, and easily leads to overestimation of the organic carbon mass in atmospheric aerosols. The group of Hering et al. [1990] showed that adsorption of gas-phase compounds is significant and must be taken into account. Another problem is the evaporation of organic compounds from filtered aerosol, especially in HVS where air flow is high [Peters et al. 1967, Tang et al. 1994, Turpin et al. 2000]. Attempts have been made to solve this problem by using two quartz filters, one for the aerosols and one as the back-up filter, or using teflon as the aerosol filter and quartz as the back-up [Turpin et al. 1994, Kirchstetter et al. 2001]. However, even this approach does not eliminate all problems.

Oxidation is a very important issue in off-line sampling techniques. Although in impactors and cyclones gas-phase oxidants can be removed by denuders [Williams et al 1990], this is not possible in HVS because of the high air flow. Compounds such as low troposphere ozone, nitrogen oxides, hydroxyl radical, and sulfuric acid may oxidize the sample compounds, causing the qualitative and quantitative determination of chemical composition to be incorrect.

One way to minimize the drawbacks of off-line techniques is on-line coupling of sampling and analysis. The combination of analytical technique with particle-into-liquid sampling (PILS), introduced by Weber et al. [2001], has recently become a useful tool for the collection and analysis of aerosols on-line. The sampling device has been modified for ground and airborne measurements of water-soluble aerosol composition [Orsini et al. 2003]. PILS combines two conventional techniques in aerosol measurements: particle growth in oversaturated water vapor and impaction on quartz plate (Figure 5). The device has been used for the determination of ion composition in atmospheric aerosols by coupling it on-line with ion chromatography [Weber et al. 2001, Orsini et al. 2003, Kondo et al. 2007], but also for the determination of water-soluble organic carbon by coupling it with a total organic carbon analyzer (TOC) [Sullivan et al. 2004]. Recently, PILS was combined simultaneously with TOC and ion chromatographs (IC) to obtain more analytical data with high time resolution [Timonen et al 2010].

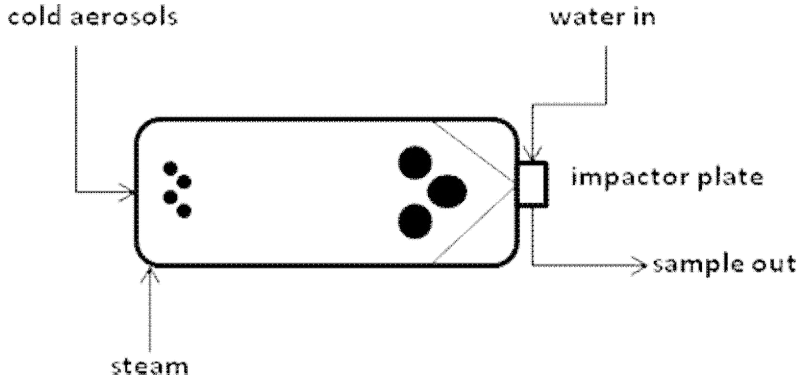

Figure 5. Schematic picture of particle-into-liquid sampler.

The most useful feature of PILS is that it produces continuous liquid aerosol sample flow, which in theory can be introduced to any analytical device. To connect PILS to HPLC-MS was one of the aims of this study and it will be discussed below in detail.

In addition to the indirect techniques discussed above, direct mass spectrometry of atmospheric aerosols is now possible. Aerosol mass spectrometry (AMS) and laser desorption ionization mass spectrometry have successfully been applied in many field campaigns and chamber experiments providing on-line information on aerosol organic carbon composition [Baltensperger et al. 2005, Allan et al. 2006, Canagaratna et al. 2007, Alfarra et al. 2007, Jimenez et al. 2009]. In the case of AMS, a single particle or group of particles is fed directly to the mass spectrometer ionization source after thermal desorption. This is, in practice, the main disadvantage of the AMS, since high temperature of thermal desorption is combined with electron impact ionization (EI). The harsh conditions lead to a rather primitive mass spectrum that is scanned only up to 100 m/z. Detailed examination is impossible, since spectra of thousands of compounds are combined and compressed into one. Recently, a different approach to ionization in AMS was introduced. Laser desorption and photo ionization combined with time-of-flight mass spectrometry (ToF-MS) was found to be a promising tool for extracting more detailed information from aerosol spectra [Laitinen et al. 2009, 2010].

The information on chemical composition, especially on organic compounds, gleaned from particles smaller than 100 nm is highly important if we are to understand completely the nucleation and growth of aerosols taking place in the atmosphere [Metzger et al 2010]. Excluding direct mass spectrometric analysis, determination of the chemical composition of nanometer-size particles has seldom been attempted because of the challenging sample collection and low mass of organic carbon [Ochiai et al. 2007, Saarikoski et al. 2005, 2008].

A differential mobility analyzer (DMA) was just recently employed for the size separation of ambient atmospheric aerosols before filter sampling [Laitinen et al. 2010]. With the use of DMA, particles under 100 nm can be collected on the filter. However, the total aerosol mass after collection time of even several days may be as small as a few tens or hundreds of nanograms, which means that adsorption of gas-phase compounds on the filter may account for most of the organic carbon mass. Even though the partitioning of gas-phase compounds to aerosol phase is a well known fact [Storey et al. 1995, Pankow 1997], quantitative determination of the contribution of gas-phase is not conducted for the majority of atmospherically relevant species and thus it was one of the aims of the present study.

3.2 Sample treatment

Since almost all atmospheric aerosol samples are collected on filters, this section will focus on the common extraction techniques for aerosol filters. One of the most popular techniques is sonication-assisted extraction, which utilizes cavitation to improve the contact between solid and liquid phases. High local temperatures and pressures are produced due to the compression and expansion of the bubbles formed as sound waves pass through the matter [Vinatoru et al. 2001]. There are two ways of performing ultrasonically assisted extraction: statically assisted (SAE) and dynamically assisted (DSAE).

In SAE, pieces of filter are placed in a test-tube or beaker filled with an extraction solvent and subjected to an ultrasonic bath [Surratt et al. 2006, Krivacsy et al. 2001]. The procedure can be repeated several times to prevent saturation of the extraction solvent [Kallio et al. 2003]. Saturation of the solvent does not occur in DSAE because fresh solvent is pumped through the extraction chamber, which is usually made of PEEK, during the whole procedure [Kallio et al. 2006]. This extraction method is fast, not matrix or analyte dependent, and inexpensive. It can also be relatively easily coupled on-line with liquid chromatography [Kivilompolo et al. 2009].

Soxhlet extraction is commonly applied for filter samples. In this technique, unlike in SAE, free radicals are not produced. Organic constituents of aerosols can be successfully extracted with Soxhlet with good recovery [Ray et al. 2005, Li et al. 2006]. However, Soxhlet is time consuming (12-24 h) and requires considerable amounts of solvent and glass ware. This technique is not therefore the best choice if the number of samples is high, as is usually the case.

The extraction solvent is usually chosen according to the analytes of interest and the analysis technique. Methylene chloride is suitable for most applications. Different combinations of methylene chloride with hexane and acetone are not better than pure methylene chloride [Jaoui et al. 2001].

Other extraction techniques are little used in aerosol analysis since they are such that samples may be destroyed. Techniques that operate at high temperatures and pressures (supercritical fluid extraction (SFE), pressurized hot water extraction (PHWE), accelerated solvent extraction (ASE), microwave digestion) may lead to oxidation of the sample. Also, they require expensive instrumentation and need to be optimized by well-trained personnel. SFE nevertheless has been

used together with GC-MS to extract and analyze organic compounds in atmospheric aerosols [Hansen et al. 1995, Castells et al. 2003], and elemental analysis has been done using microwave digestion and inductively coupled plasma mass spectrometry [Hueglin et al. 2005].

After extraction, aerosol samples are usually concentrated either by evaporation of solvent with rotavapor or by a stream of nitrogen. Nitrogen protects the sample from oxidation and ensures that volatile species remain in the sample. In most studies, concentrated extracts are subjected to analysis without clean-up. However, derivatization will normally be required if analysis is by GC. The most popular derivatization procedure is silylation, but alkylation is common as well [Jaoui et al 2001, 2003].

Recently, more advanced sample treatment methods have been introduced to meet the criteria of analytical techniques. For instance, comprehensive two-dimensional GC [Kallio et al 2006] and sample cleanup have been introduced to prevent the overlap of large amounts of saturated hydrocarbons with compounds of interest in GC analysis. In a study of Shimmo et al. [2004], extracted aerosol samples were separated by LC before analysis by GC, with the whole procedure done on-line in a closed system.

Selective clean-up is particularly important in the analysis of aerosols by HPLC-MS since ion suppression may occur if separation is not sufficient. Quantitation of compounds could then become impossible. Solid-phase extraction offers an easy, cheap, and fast way to prepare aerosol samples in suitable form for HPLC-MS. Previously SPE was used mainly for fractionation and concentration of aerosol samples extracted by SAE or SLE [Kallio et al. 2003, Asa-Awuku et al. 2008]. The benefits of SPE, especially the possibility of on-line coupling [Kivilompolo et al. 2009], need to be exploited in aerosol analytics, and use of SPE for sample treatment was explored in this study.

3.3 Analysis of aerosol samples

No universal technique is available for the simultaneous qualitative and quantitative analysis of all groups of organic compounds. Several techniques with different requirements (volatility, polarity, etc.) have to be employed, and compromises are unavoidable. Thus, complete investigation of atmospheric aerosol chemical composition is highly challenging if not impossible. Fortunately, full investigation is seldom needed, since compounds of interest will usually belong to just one or two groups (e.g., carboxylic acids and aldehydes).

Gas chromatography-mass spectrometry is the preferred technique for the elucidation of aerosol chemical composition, mostly because together with electron impact ionization it can provide valid spectra for library search. Even though GC is directly suitable for only a small number of compounds, derivatization can significantly increase this number.

GC is the usual choice for the determination of compound distribution between aerosol phase and gas phase in chamber experiments [Jaoui et al. 2001, 2003, Edney et al. 2005, Fisseha et al. 2004]. GC has also led to the identification of polymers among the major compounds in aerosols [Kalberer et al. 2004]. Formation of secondary organic aerosols from oxidation of isoprene has been shown by GC-MS investigation [Claeys et al. 2004]. Likewise, correlations between photooxidation products of monoterpene acids and new particle formation events have been demonstrated by GC-MS [Kavouras et al. 1999].

Solvent-extracted samples are usually injected to the GC-MS as such [Simoneit et al. 1999, Rissanen et al. 2006]. Thermal desorption GC has also been applied for direct aerosol sample introduction [Waterman et al. 2000, Falkovich et al. 2001, Hays et al. 2003]. Thin layer chromatography (TLC) prior to GC-MS was used by Almeida Azevedo et al. [1999]. TLC allowed the separation of aerosol constituents by groups, simplifying their analysis by GC-MS.

Since secondary atmospheric aerosols contain many highly oxidized compounds, such as carbonyls and carboxyls, their examination by GC-MS is time consuming. Derivatization is not required in HPLC, and HPLC coupled with mass spectrometric detector via atmospheric pressure ionization source (ESI, APCI, APPI) has become popular. Chemical composition of water-soluble organic carbon compounds in aerosols has been investigated by HPLC-MS [Anttila et al. 2005, Glasius et al. 1999, Reinnig et al. 2008, Warnke et al. 2006, Jakober et al. 2006].

Formation of aerosol acids by oxidation of cyclic terpenes with ozone has been demonstrated by the same method [Glasius et al. 2000]. Amines and aldehydes, which are other important compounds in aerosols for aerosol formation, are easily analyzed by HPLC-MS.

With comprehensive two-dimensional chromatography (GC*GC, LC*LC) now more popular, and with commercial devices recently available, application has also been made to the analysis of atmospheric aerosols. PAH compounds have been quantitatively determined in urban aerosols by GC*GC-FID [Kallio et al. 2003], and terpene compounds together with several ketones, aldehydes, alcohols, and acids have been identified by GC*GC-ToF [Kallio et al. 2006, Hamilton et al. 2004]. Direct thermal desorption GC*GC-ToF has been used to determine within-day variations of selected compound groups (nitriles, methylesters, alkyl benzenes, hopanes, etc.) in PM10 aerosols [Schnelle-Kreis et al. 2005], and also for in-situ measurements of organic aerosols [Goldstein et al. 2008]. To simplify the identification procedure in GC*GC-TOF, Vogt et al. [2007] designed software to separate compounds found in aerosols into groups according to their characteristic mass fragmentation and retention times.

The use of internal standards and scanning mass spectrometry in LC and GC analysis is highly recommended. New compounds are continually being synthesized, and old chromatograms can be reviewed to determine compounds not previously identified.

4 EXPERIMENTAL

Chemicals, material, equipment, sampling sites, synthesis of reference compounds, sample preparation, and analytical conditions in the experiments are described in this chapter. More detailed information can be found in Papers **I-V**.

4.1 Chemicals, sampling sites, and conditions

Chemicals and materials are listed in **Table 1** and sampling sites together with sampling periods in **Table 2**.

Table 1. Chemicals and materials used in the experiments (**I-V**)

Compound	Manufacturer/supplier	Comments	Paper
(+)-Pinanediol	Aldrich	Reagent	I
1,1'-Binaphthyl	Acros Organics	Internal standard	I,IV-V
18-Crown-6-ether	Sigma-Aldrich	Reagent	I
2,4-Dichlorobenzoic acid	Sigma-Aldrich	Standard compound	II,IV
2-Propanol	Lab-Scan	Solvent, HPLC grade	I
2-Pyridylbenzoimidazole	Sigma-Aldrich	Internal standard	IV
3-Hydroxyglutaric acid	Anal. Chem. Lab	Standard compound	III,IV
Acetic acid	J.T.Baker	Solvent, HPLC grade, glacial, 99-100%	III-V
Acetone	J.T.Baker	Solvent, 99.7%	V
Acetonitrile	Lab-Scan	Solvent, HPLC far UV	II-IV
Adipic acid	BDH Chemicals	Standard compound	III,IV
Azelaic acid	Fluka	Standard compound	II,IV
Benzaldehyde	Accu Standard Inc	Standard compound	II,IV
Benzoic acid	Schering-Kahlbaum	Standard compound	III,IV
BSTFA	Sigma-Aldrich	Bis(trimethylsilyl)trifluoroacetamide	II-IV
Capryllic acid	Sigma-Aldrich	Standard compound	III
Carbon dioxide	AGA	Dry ice for cooling	V
Cinnamaldehyde	Sigma-Aldrich	Internal standard	IV
cis-Pinonic acid	Sigma-Aldrich	Standard compound	I-IV
Decafluorobenzophenon	Sigma-Aldrich	Internal standard	I,II,IV
Deuterochloroform	Euriso-Top	99.8%+0.03% TMS	V

Table 1. *continued*

Compound	Manufacturer/supplier	Comments	Paper
Dichloromethane	Lab-Scan	Solvent, HPLC grade	II,III,V
Diethylamine	Sigma-Aldrich	Standard compound	IV
Dipropylamine	Fluka	Standard compound	IV
D-Mannose	Sigma-Aldrich	Standard compound	IV
Ethanol	Primalco Oy	Solvent, 99.5 wt%	V
Ethyl acetate	Lab-Scan	Solvent, 99.8%	II,V
Ethylenediamine	Sigma-Aldrich	Standard compound	IV
Formic acid	Merck	Solvent	II
Glycerol	Sigma-Aldrich	Reagent	I-III
Helium	AGA	Carrier gas, purity 99.996%	V
Heptanal	Accu Standard Inc	Standard compound	II,IV
Hexanal	Accu Standard Inc	Standard compound	IV
Isopropylamine	Sigma-Aldrich	Standard compound	IV
Isopropylaniline	Sigma-Aldrich	Standard compound	IV
Levoglucosan	Sigma-Aldrich	Standard compound	IV
Maleic acid	Fluka	Standard compound	III,IV
Malic acid	Fluka	Standard compound	III,IV
Malonic acid	Fluka	Standard compound	III,IV
Mandelic acid	BDH Chemicals	Standard compound	III,IV
Methanol	J.T.Baker	Solvent, HPLC grade	I,III,IV
n-Hexane	J.T.Baker	Solvent, 99%	IV-V
Nonanal	Accu Standard Inc	Standard compound	II,IV
n-Propanol	Rathburn Chemicals	Solvent, HPLC grade	I
Octanal	Accu Standard Inc	Standard compound	II,IV
Oleic acid	Sigma-Aldrich	Standard compound	IV
Palmitic acid	Sigma-Aldrich	Standard compound	II,IV
para-Aminophenol	Sigma-Aldrich	Standard compound	IV
Pentafluorobenzyl bromide	Sigma-Aldrich	Reagent	I
Periodic acid	Merck	Reagent	I
Phosphoric acid	Merck	Reagent, 85%	I,II
Pinic acid	Sigma-Aldrich	Standard compound	I-III,IV
Pinonaldehyde	Anal. Chem. Lab	Standard compound	I,IV
Potassium iodide	Merck	Reagent	I-III,V
Pyridine	J.T.Baker	Solvent	II-IV
Quartz filters I	Munktell	240 mm diameter	V
Quartz filters II	Whatman	grade QMA, 4.7 cm	IV
Sebacic acid	Fluka	Standard compound	III,IV

Table 1. *continued*

Compound	Manufacturer/supplier	Comments	Paper
Silica gel 60	Merck	Flash chromatography, 0.04-0.063 mm	V
Sinapic acid	Sigma-Aldrich	Standard compound	III
Stearic acid	Fluka	Standard compound	II,IV
Tartaric acid	Fluka	Standard compound	III,IV
Teflon filters	Millipore	Fluoropore, type FALP, 4.7 cm	IV
TLC aluminum sheets	Merck	20x20 cm, silica gel 60 F254	V
Toluene	J.T.Baker	Solvent	IV
Tridecanal	Accu Standard Inc	Standard compound	IV
Tripropylamine	Sigma-Aldrich	Standard compound	IV
Undecanal	Accu Standard Inc	Standard compound	II
Vanillic acid	Fluka	Standard compound	III,IV
XAD-2 resin	EGA-Chemie	Reagent, polystyrene-divinylbenzene	I-III
Zinc	Sigma-Aldrich	Reagent	V
α-Pinene	Fluka	St ndard compound	I
β-Caryophyllene	Sigma-Aldrich	Standa d compound	V
β-Caryophyllene aldehyde	Anal. Chem. Lab	Standard compound	IV
β-Caryo hyllinic acid	Anal. Chem. Lab	Standard compound	II
β-Nocaryophyllene aldehyde	Anal. Chem. Lab	St ndard compound	II,IV

Table 2. Sampling systems, sampling sites, and time periods during which samples were collected.

Type	Sampling site	Time period	Paper
PILS	SMEAR II, Laboratory	April 23-28, 2007	I
PILS	SMEAR II	August 13-16, 2007	II
PILS*	Laboratory	February 4-10, 2010	III
DMA-quartz/teflon	SMEAR III	February 18 - April 19, 2010	IV
HVS, quartz	SMEAR II	Spring 2003	V

*- on-line and off-line

Descriptions of sampling sites

SMEAR II: Hyytiälä, Finland (61°51´N, 24°17´E, 180 m above sea level), 230 km north of Helsinki. Forest consists of Scots pines (*Pinus sylvestris* L.) 40-50 years old, homogeneously spread through 200 m in all directions from the measurement site [Kulmala et al 2001].

SMEAR III: Helsinki, Finland (60° 12' N, 24° 57' E, 26 m above sea level), heterogeneous surroundings consisting of buildings, parking lots, roads, patchy forest, and low vegetation [Järvi et al. 2009].

Laboratory: Laboratory of Analytical Chemistry, University of Helsinki, Finland (60° 12' N, 24° 58' E, 40 m above sea level), surroundings as at SMEAR III

4.2 Synthesis of reference compounds

The structures of compounds synthesized during the study are shown in Figure 6 (except for β-caryophyllinic acid, whose structure was not confirmed by NMR).

Pinonaldehyde was synthesized by oxidation of (1S,2S,3R,5S)-(+)-pinanediol with periodic acid [Glasius et al. 1997]. The structure was confirmed by EI-MS. For the synthesis of β-caryophyllinic acid, 10% solution of β-caryophyllene in dichloromethane was cooled to -68 °C (dry ice in ethanol). Ozonolyzed air (dried, purified) was bubbled through the solution at a flow rate of 10 l/h. Reaction time needed for the complete oxidation was 30 min. The reaction mixture was extracted twice with 10 ml of 5% ammonia solution in water. Aqueous fractions were combined and extracted with MAX material (**Paper II**). The structure was confirmed by ESI-MS and EI-MS after silylation.

3-Hydroxyglutaric acid was synthesized as described elsewhere [Claeys et al. 2007]. The reaction product had to be purified with SAX, however (**Paper III**). The structure was confirmed by ESI-ITMS and EI-MS after silylation.

A more precise description of the synthesis of β-caryophyllene aldehyde and β-nocaryophyllene aldehyde is presented in **Paper V**. Briefly, β-caryophyllene solution was first oxidized with a stream of ozone in dichloromethane at -68 °C. Later, reduction reaction was done with zinc powder and acetic acid. Aldehydes were extracted by LLE with dichloromethane. Fractionation was done by flash chromatography. Fractions were analyzed by TLC and those containing only one compound were combined and dried. The structures were confirmed by EI-MS, ESI-ITMS, and NMR.

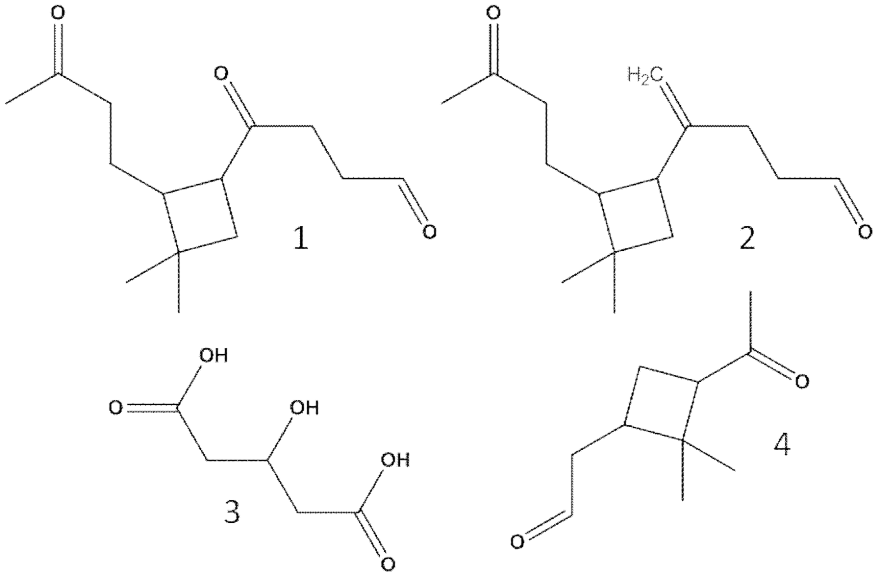

Figure 6. Structures of compounds synthesized during this study. **1** β-nocaryophyllene aldehyde, **2** β-caryophyllene aldehyde, **3** 3-hydroxyglutaric acid, **4** pinonaldehyde.

4.3 Devices

The commercial instruments used in the studies are listed in **Table 3**.

Table 3. Commercial instruments used in the research.

Device/Instrument	Model and manufacturer	Comments	Paper
PILS	Applikon Analytical, The Netherlands		I-III
Peristaltic pump	Watson Marlow 205S, USA	Coupled with PILS	I-III
Denuder	URG, USA	Three-channel, 242 mm length	I-III
Cyclone	PM2.5, URG, USA	Coated with vacuum grease	I-III
Gas chromatograph	Agilent 6890N, USA	Split/splitless, on-column	I-V
Mass selective detector	Agilent 5973N, USA	Quadrupole, 70 eV	I-V
Mass spectrometer	Bruker Esquire 3000 plus, USA	Ion trap	I-V
Liquid chromatograph	Hewlett-Packard Series 1100, USA		II-IV
Pump	Jasco PU-980, Japan	On-line system	III
Ten-port valve	C2-1000EP, VICI Valco, USA	On-line system	III
Three-way valve	30-15 HF4-HT, High Pressure Equipment, USA	On-line system	III
Ozone generator	Fisher, UK	Corona discharge	V
Ultrasonic bath	Branson 3510, Branson Ultrasonics, USA		V
Spectrometer	Varian Inova 500, Varian, USA	NMR analysis	V
Mass spectrometer	MicrOTOF, Bruker Daltonics, Germany	ESI-TOF	V
Sonifier	Branson, S-250 A, USA	Titanium alloy micro tip (3 mm)	V

The experimental variables that affect the DMA collection, such as sheath air flow (Qsh), aerosol flow (Qs), and applied voltage (V), were adjusted for the collection of 50, 40, and 30 nm particles [Winklmayr et al. 1991]. Before size segregation, the sampled particles are brought to a known charge distribution [Wiedensohler et al. 1988] with an Am-241 alpha-source (60 MBq). More precise information about DMA sampling is presented elsewhere (**IV**). Figure 7 shows a schematic representation of the DMA-assisted collection system.

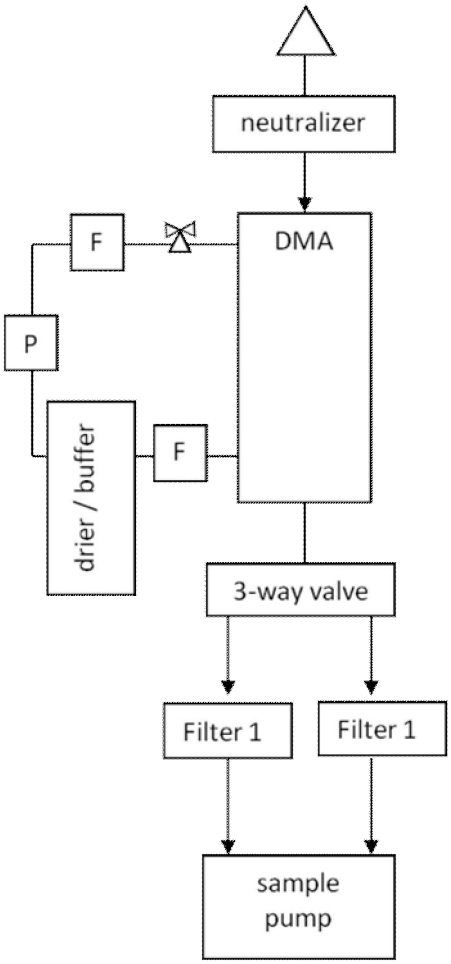

Figure 7. Description of the aerosol collection system. P and F indicate a pump and high efficiency particulate filters (HEPA) in the sheath flow of the DMA.

4.4 Sample preparation: off-line and on-line

SAE (**V**) and DSAE (**IV**) were chosen for extraction of filter samples in the off-line analysis. A 50:50 v/v mixture of acetone and hexane was used as extraction solvent. PILS samples were initially (paper **I)** extracted by LLE with dichloromethane after pH adjustment (pH 1.5). In the case of DSAE, extraction time was from 20 to 40 min and the solvent flow rate was 0.5 ml/min. All samples were concentrated under a gentle stream of nitrogen since rotavaporation could affect volatile analytes.

Later, two types of solid-phase extraction materials, HLB (StrataX, 3 ml, 30 mg, Phenomonex, USA) for aldehydes and MAX (OasisMAX, 1 ml, 30 mg, Waters Corp., USA) for acids, were tested for the extraction of PILS samples (**Paper II)**. Only MAX performed satisfactorily and all PILS samples were extracted with MAX. The sample pretreatment procedure included the following steps: activation (2 ml of methanol), equilibration (2 ml of water), sample addition (10 or 20 ml), and elution with 1 ml of 2% formic acid in methanol. In all the extractions, gravitational force was used without additional vacuum.

On-line SPE of PILS samples was performed with the setup shown in **Figure 8**. A more precise description of the on-line coupled PILS-SPE-LC-MS procedure can be found in **Paper III**. Briefly, a column (30 mm x 2.1 mm I.D.) was packed with SAX material (Isolute, IST, UK) and, before the sampling, it was washed with methanol and water (on-line). The valve position was then changed to guide the PILS sample through the SPE for the two-hour sampling time. At the end, the valve was switched to guide the HPLC eluent mixture through the loop (500 µl of 10% acetic acid) and SPE trap to the HPLC-MS. For comparison, half of the on-line PILS samples were extracted by off-line SPE (HyperSep, 100 mg/1 ml, Thermo Electron Corporation, USA) and analyzed by GC-MS after derivatization (**Paper III**).

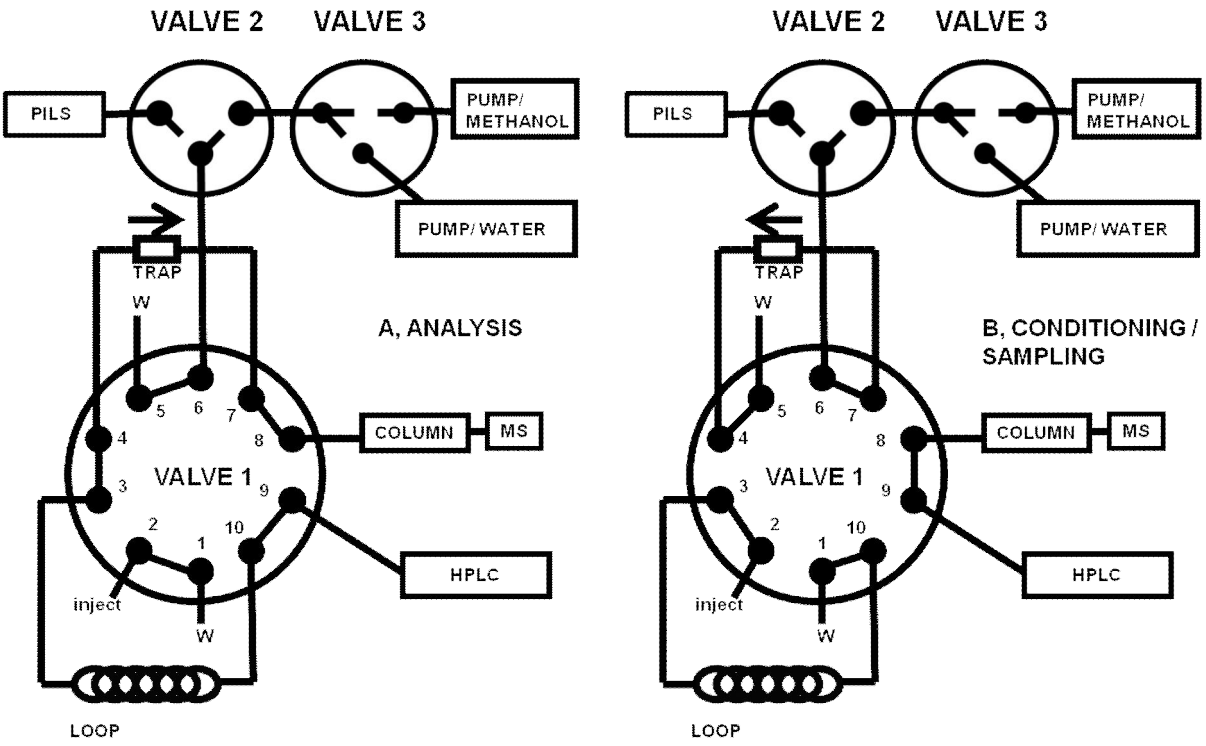

Figure 8. Schematic representation of the constructed on-line coupled PILS-SPE-HPLC-MS system. (A) Procedure for sample analysis and (B) procedure for conditioning the trap and for sampling.

4.5 Analysis conditions

The GC and HPLC columns that were used are listed in **Table 4** together with their dimensions Table 4 also gives the analytical conditions employed with the columns and the analytes studied.

Table 4. GC and HPLC columns with analytical conditions, particle dimensions, and analytes.

Column type/ Manufacturer	Analytical conditions	Dimensions/ particle size	Paper/ Analytes
HP-5, Hewlett Packard, USA	60 °C (2 min)-10 °C/min- 300 °C (10 min)	29 m x 0.25 mm x 0.25 µm retention gap: 2 m, 0.53 mm	I, oxidation products of α-pinene and β-caryophyllene, V II, organic acids
Xbridge Shield, RP-18 Waters Corp., USA	linear gradient from 10 to 100% B in 30 min A: 0.1% formic acid in water, B: ACN	2.1 mm x 150 mm, 5 µm	II, organic acids
Xbridge, RP-18 Waters Corp., USA	0-2 min 100% A, 2-5 min 50% A, 5-7.5 min 25% A 7.5-15 min 100% B; A: 1% acetic acid in water B: 1% acetic acid in ACN	4.6 mm x 75 mm, 2.5 µm	III, organic acids
DB5-MS Agilent, USA	60 °C (4 min)- 6 °C/min-140 °C (6 min)- 5 °C/min- 190 °C (4 min)- 5 °C/min- 210 °C-20 °C/min-270 °C (5 min)	30 m x 0.25 mm x 0.25 µm retention gap: 3 m, 0.53 mm	III, organic acids IV, acids, polyols
HP1701, Hewlett Packard, USA	60 °C (5 min)-5 °C/min- 280 °C (10 min)	18 m x 0.25 mm x 0.25 µm retention gap: 3 m, 0.53 mm	V, oxidation products of β-caryophyllene
Xbridge, RP-18 Waters Corp., USA	isocratic 1:1 water:2% ammonia in ACN	4.6 mm x 75 mm, 2.5 µm	IV, amines
Atlantis C18 Waters Corp., USA	90% A (2 min), 2-4 min 10% A, 4-6 min 100% B (7 min) A: 2% acetic acid in water, B: 2% acetic acid in ACN	2.1 × 150 mm, 3 µm	IV, aldehydes

5 RESULTS AND DISCUSSION

The presentation of the results of the work is divided into two parts. The first part summarizes the results of instrumental developments, including optimization of off-line and on-line sampling. Part two is focused on methodological developments and summarizes the results relevant to the chemical composition of atmospheric aerosol particle samples.

5.1 Instrumental developments

It is well recognized that sampling is prone to error, and these errors cannot be tracked or corrected later during the analytical procedure. Mainly for this reason, a large part of the present research was focused on aerosol sampling, including off-line and on-line PILS sampling and filter sampling with DMA as a size separation device. Off-line PILS sampling will be described in conjunction with the on-line coupled setup. The advantages of DMA as a size separator before filter sampling will be discussed.

5.1.1 Optimization of particle-into-liquid sampling

The focus of **Papers I**, **II,** and **III** was the modification and optimization of the PILS sampling system, to make it applicable not only to on-line determination of major chemical compounds in aerosol samples, but also to the determination of less abundant species. At the beginning, ambient aerosol samples collected with PILS were analyzed by conventional techniques to elucidate the concentration level of less abundant compounds. This information then allowed estimation of the minimum sampling time needed for the collection of sufficient amount of organic mass. GC-MS was chosen as analytical technique and LLE for sample treatment. To simplify the task, only oxidation products of α-pinene (pinonaldehyde, pinic acid, *cis*-pinonic acid) were quantified. As a result, two-hour sampling provided a sufficient amount of sample for quantitative determination. Typical extracted ion chromatograms recorded from two-hour PILS samples are shown in **Figures 9** and **10**.

To minimize the gas-phase contribution and oxidation of samples, annular denuders with different coatings were added between the cyclone and PILS sampling line. XAD was chosen for the removal of gas-phase organic compounds, potassium iodine for scavenging of ozone, and phosphoric acid to remove basic gases, such as ammonia. To study the efficiency of the XAD denuder, a teflon filter was placed in the inlet, and the PILS sample was collected for two hours. Another sample was collected in the same way but without the XAD denuder in the line. GC-MS analysis of the samples showed that the XAD denuder was effective in removing some compounds (e.g., ethylhexanol, naphthalenone, benzothiazole, oxidized hydrocarbons). However, because many compounds were not efficiently removed from the sampling line, it was decided that two XAD denuders should be used in further experiments.

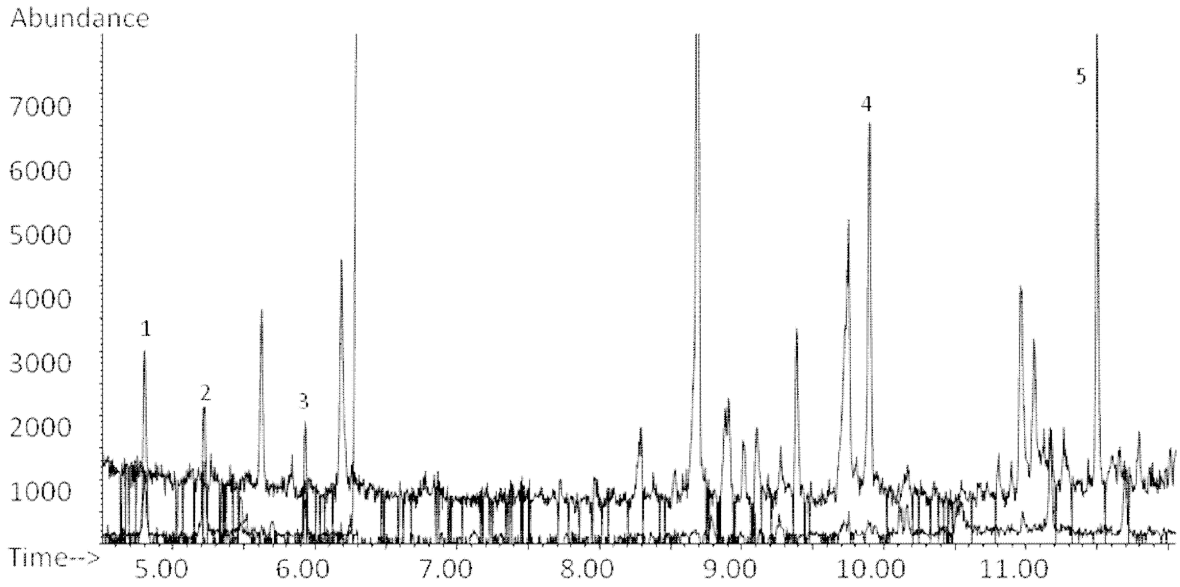

Figure 9. Typical extracted ion chromatogram of a two-hour PILS sample (Hyytiälä, April 24, 2007, collected from 10.30 am to 12.30 pm). Peaks and selected ions are 1) β-pinene (m/z 93), 2) benzaldehyde (m/z 77), 3) α-pinene (m/z 93), 4) pinonaldehyde (m/z 83), 5) norpinonaldehyde (m/z 83). From **Paper I**.

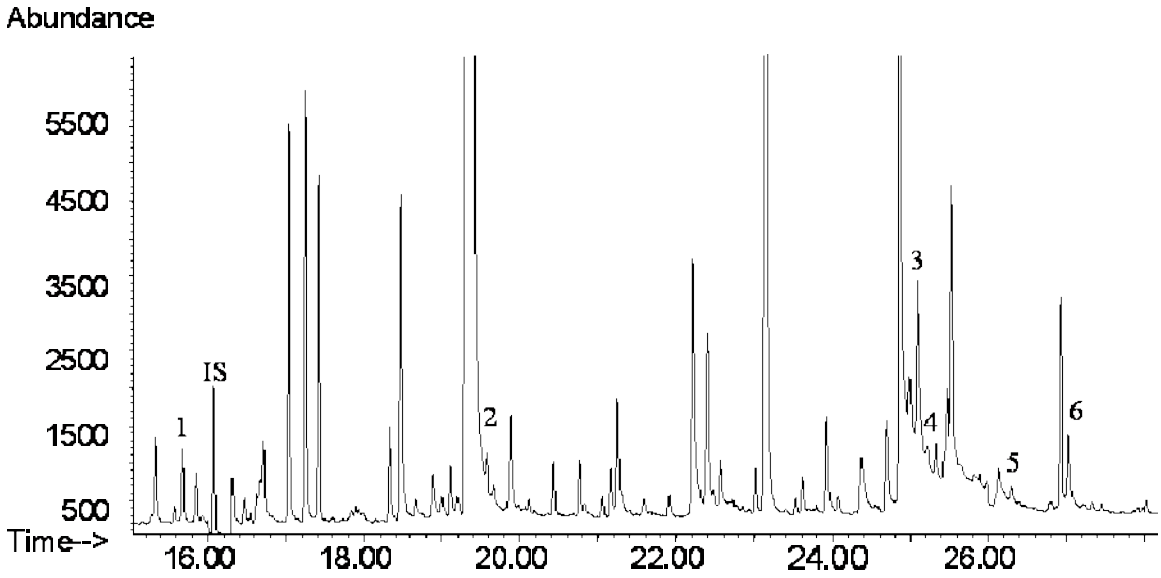

Figure 10. GC-MS (SIM) chromatogram of a PILS sample collected from 11 am to 1 pm on April 28th 2007. 1) caprylic acid; IS internal standard; 2) cis-pinonic acid; 3) palmitic acid; 4) pinic acid; 5) vanillic acid; 6) stearic acid. SIM ion groups and start times: m/z 83,181,324 (5.00 min); m/z 456 (16.00 min); m/z 83,181 (16.30 min); m/z 69,181,255,436 (24.90 min); m/z 181,347 (26.00 min); m/z 181,265 (26.90 min). From **Paper I**.

Water is the usual transport liquid in PILS, but it is not the best solvent for atmospheric aerosols since only water-soluble organic carbon can then be collected and transferred to the analytical device. The suitability of other solvents in PILS was therefore investigated (**Paper I)**. Several amphoteric alcohols (methanol, ethanol, 1-propanol and 2-propanol) were tested, but none of them worked ideally. The high tip temperature meant that most were evaporated around the impactor plate. Although 1-propanol passed through this barrier it could not be used because it degraded the PVC material of the tubings. In the end, water proved to be the only suitable solvent for PILS in the setup employed.

PILS samples were also directly injected to ESI-ITMS. As can be seen in **Figure 11**, pinic and *cis*-pinonic acid peaks could be identified by MS^2 (characteristic cleavage of carbon dioxide and water from acid molecules). This successful trial encouraged us to continue research on PILS-

MS. Later, other groups followed our idea and studied PILS-MS further [Bateman et al. 2010, Chang-Graham et al. 2011].

Because the concentrations of compounds of interest in PILS samples were too low for their quantitative determination, in a next step the samples were concentrated for aldehydes and organic acids by solid-phase extraction.

HLB and MAX (MAX is basically HLB modified with quaternary amine) were tested in the extraction of standard solutions. HLB did not extract aldehydes well; the extraction efficiencies for nine replicates were in an unacceptably wide range from 70 to 159% (**Table 5**). In contrast, anion exchange material MAX gave extraction efficiencies around 100% for all selected acids in all concentrations and sample volumes (**Table 6**).

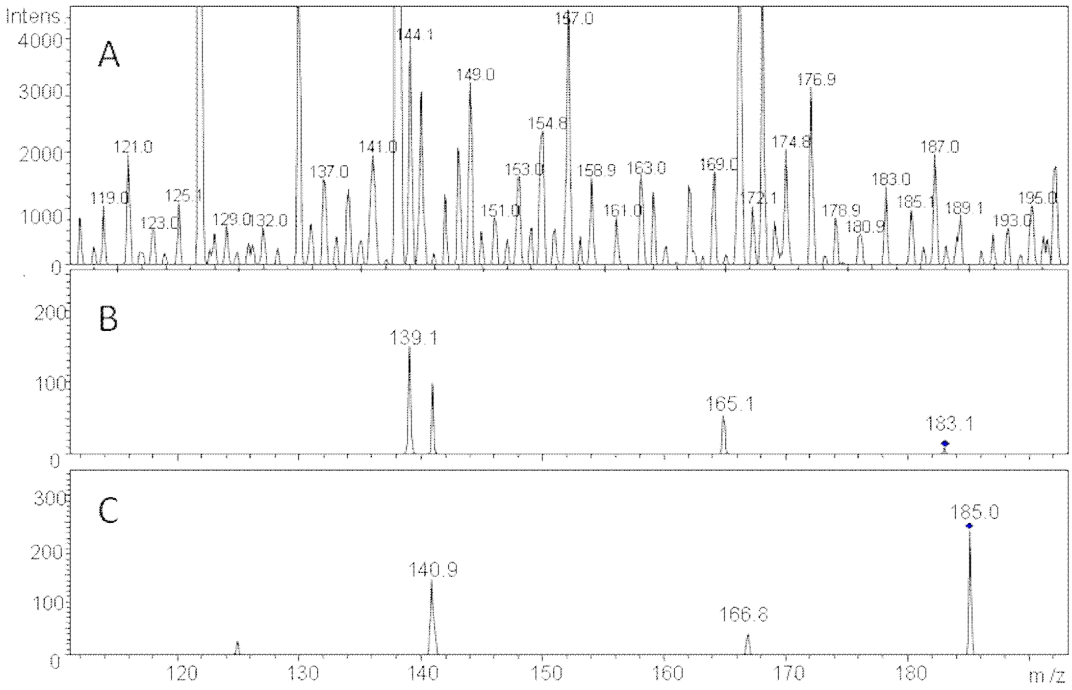

Figure 11. ESI-ITMS spectra for a directly injected PILS sample. A: 25 August 2007, from 12:00 to 13:00; MS^2 spectra from ion 183 (B) and 185 (C) in sample A. From **Paper I**.

PILS samples were extracted with MAX material and analyzed for selected acids by HPLC-MS (MS^2) (**Paper II**). The analysis revealed the presence of *trans*-pinonic acid, which has not previously been well investigated. Only in a few studies has this compound been found in biogenic aerosols, and usually the *cis*- and *trans* isomers have been quantified as their sum [Kavouras et al. 2002, Alves et al. 2002]. In all relevant studies in the literature, two peaks with the same MS profile and with very small differences in retention times have been reported for pinonic acid in real aerosol samples. Since we found only one peak for the commercially available standard of *cis*-pinonic acid (two for pinic acid standard) and since the retention times of the two peaks found from our aerosol samples differed by only one minute and gave the same MS and MS^2 spectra, we concluded that the two isomers of pinonic acid were in question in our samples.

Table 5. Solid-phase extraction efficiencies for aldehydes obtained with HLB material (%±RSD%, n=9). From Paper **II**.

Sample	β-nocaryophyllene aldehyde	pinene aldehyde	heptanal	benzaldehyde	octanal	nonanal	undecanal
125µg/L, 10ml	-	151±3	134±12	88±4	89±3	-	-
125µg/L, 20ml	-	156±2	141±3	93±6	98±5	-	-
250µg/L, 10ml	107±19	87±5	99±13	73±9	66±17	-	-
250µg/L, 20ml	-	112±6	122±4	107±7	103±8	-	-
500µg/L, 10ml	103±26	58±3	111±5	111±3	92±4	98±20	84±1
500µg/L, 20ml	105±13	69±5	95±3	90±8	76±4	127±23	89±9
1000µg/L, 10ml	137±13	93±6	71±9	82±10	70±8	97±12	73±8
1000µg/L, 20ml	163±13	113±10	74±9	83±8	80±4	159±21	96±10

Table 6. Solid-phase extraction efficiencies for acids obtained with OasisMAX material (%±RSD%, n=9). From Paper **II**.

conc µg/L	*cis*-pinic acid, 10 ml	*cis*-pinic acid, 20 ml	*trans*-pinic acid, 10 ml	*trans*-pinic acid, 20ml	*cis*-pinonic acid, 10 ml	*cis*-pinonic acid, 20 ml	azelaic acid, 10 ml	azelaic acid, 20ml
5	64.2±17.0	79.8±19.0	147.9±10.2	114.9±18.0	96.1±14.7	94.6±6.3	106.8±10.0	100.5±7.6
10	74.9±8.3	76.9±9.4	103.7±18.5	70.8±48.4	96.3±4.2	93.8±7.4	116.1±12.4	77.1±30.3
12.5	90.0±2.5	93.1±1.4	110.7±8.2	97.4±2.5	100.0±8.2	98.2±5.1	99.9±2.9	90.1±1.4
25	88.2±7.3	90.8±15.2	88.7±5.5	89.3±6.6	98.9±2.7	99.6±6.5	97.5±7.6	93.3±6.0
50	93.5±7.6	99.4±1.3	82.7±4.9	91.0±12.5	95.7±6.0	99.6±2.1	91.2±4.7	92.8±2.0
100	109.8±6.4	109.8±8.0	94.0±4.9	99.8±9.6	108.5±5.3	111.6±8.4	95.0±3.9	93.5±9.4

5.1.2 On-line coupling of sampling, sample treatment, and liquid chromatography-mass spectrometry

The reliability of the total analysis can be improved by combining the sample treatment steps with the final separation and detection. On-line coupled systems reduce the risks for analyte losses and contamination from external sources. Typically, better repeatability and reliability are achieved as well. One of the aims of this research was to build an on-line system that included not only sample treatment and analysis but also sampling. Accordingly, PILS was coupled to HPLC-MS via an SPE trap. The scheme of the valve system is shown in **Figure 8**. All the connections were done with PEEK capillaries (0.5 mm I.D.) except the tubing for the HPLC effluent, which was stainless steel. As SAX material requires methanol and water washes between use, a separate pump was added to the system via a three-way valve. Thus conditioning of the trap was on-line too. Different solvent mixtures were tested as an extraction solvent. Concentrations of formic and acetic acids varied from 1 to 10%, and concentration of organic modifier, methanol or acetonitrile, from 1 to 5%. Since the volume of the loop for extraction solvent was 500 µl, the elution strength had to be high enough to elute all trapped analytes but low enough to ensure sufficient HPLC separation. In the end, acetic acid without organic additive was selected in concentration of 10%. The elution was facilitated by carrying it out in

opposite direction to sampling. The operation sequence of on-line coupled PILS-SPE-HPLC-MS is shown in **Table 7** (valve numbers follow those used in Figure 8).

Table 7. Operation sequence of on-line coupled PILS-SPE-LC-MS (sampling time 2 h).

Time (min)	**Parameter**	**Value**	**Event**
0	Valve 1	Conditioning	Cleaning the trap with methanol
	Valve 3	Methanol	
	Valve 2	Wash	
4	Valve 3	Water	Cleaning the trap with water
8	Valve 2	Sampling	PILS sampling
128	Loop	500 µl	Filling the loop manually with 10% acetic acid
	Start HPLC-MS analysis	10 µl of water	Injection and recording of data
	Valve 1	Analysis	
130	Valve 1	Conditioning	Starting the new cycle

The constructed on-line system was tested with standard solutions by slowly injecting dilute solutions to the capillary that connected PILS to the main valve. Recoveries were about 80%, and no breakthrough of compounds was observed. Memory effects were noticeable only for azelaic and sebacic acids. However, their peak areas in blank samples were always less than 5% of those obtained for the lowest concentrations used in calibration.

For comparison, half of the standard and PILS samples analyzed on-line were also subjected to off-line analysis. SPE with SAX material was used for the sample treatment and, after the evaporation and derivatization, samples were analyzed by GC-MS. Limits of detection and quantitation, correlation coefficients, and P-values for the two techniques are shown in **Table 8**.

Table 8. Comparison of on-line PILS-SPE-HPLC-MS and off-line PILS-SPE-GC-MS.

Acid	On-line			Off-line			P value
	r^2	LOD,ng	LOQ,ng	r^2	LOD,ng	LOQ,ng	
Adipic	0.935	0.9	2.8	0.995	0.04	0.14	0.822
Hydroxyglutaric	0.948	0.7	2.1	0.994	0.02	0.06	0.199
Mandelic	0.971	0.3	0.8	0.998	0.04	0.16	0.177
Vanillic	0.948	0.2	0.5	0.998	0.04	0.16	0.176
cis-Pinonic	0.931	0.2	0.6	0.997	0.06	0.20	0.050
Pinic	0.995	0.1	0.3	0.995	0.04	0.12	0.109
Azelaic	0.963	0.1	0.2	0.992	0.02	0.08	0.074
Sebacic	0.981	0.1	0.2	0.992	0.02	0.08	0.271

In the case of on-line PILS-SPE-HPLC-MS, manual sample treatment could be avoided, and the whole analysis took place in a closed system. Since analysis time with the on-line system was only 25 min, compared with 3 h with the off-line system, small differences in analytical parameters can be forgiven.

5.1.3 Sampling with a differential mobility analyzer

To determine the contribution of the gas-phase adsorption in sampling done with a DMA, amounts of compounds found on a gas-phase filter were divided by the amounts found on a filter collecting both phases (**Paper IV**). Quartz and teflon filters were tested. For the comparison of the results, absolute amounts of aerosol-phase compounds were divided by the sample volume in cubic meters.

Gas-phase compounds contributed significantly to the organic carbon mass found on the filters. For some compounds as much as 100% of the mass had originated from the gas phase (**Table 9**). It is imperative, therefore, that in the collection and analysis of nanometer-sized particles, the effect of gas phase on the results should be taken into account. Our easily constructed system with parallel filters of quartz or teflon worked well for this purpose.

Adsorption of gas-phase compounds on the filters has been found to depend on their vapor pressure [Pankow 1994, Kirchstetter et al. 2001]. Our results did not always follow this

correlation. For example, adsorption of pinic and *cis*-pinonic acids did not show dependence on vapor pressure (pinic<*cis*-pinonic), and nor, in general, did other compounds. This might have been due to deviations in the analytical and sampling methods, which could not be taken into account because a parallel DMA collection system was not available to us.

Adsorption of levoglucosan (vapor pressure 24.10 μPa) and mannose (vapor pressure 2.44 μPa) showed good correlation with vapor pressure on both filter materials (**Figure 12**). For teflon this result is surprising, since teflon is nonpolar in nature. The behavior on teflon might be explained by the adsorption of gas-phase polyols onto already collected aerosol particles that serve as an additional filtering surface. In other words, the collected aerosol layer behaves like a gas chromatographic stationary phase, with dipole and hydrophobic interactions, and thus adsorbs gas-phase compounds in a similar manner to quartz material. The presence of aerosol layer could be another reason for the vapor-pressure independent adsorption.

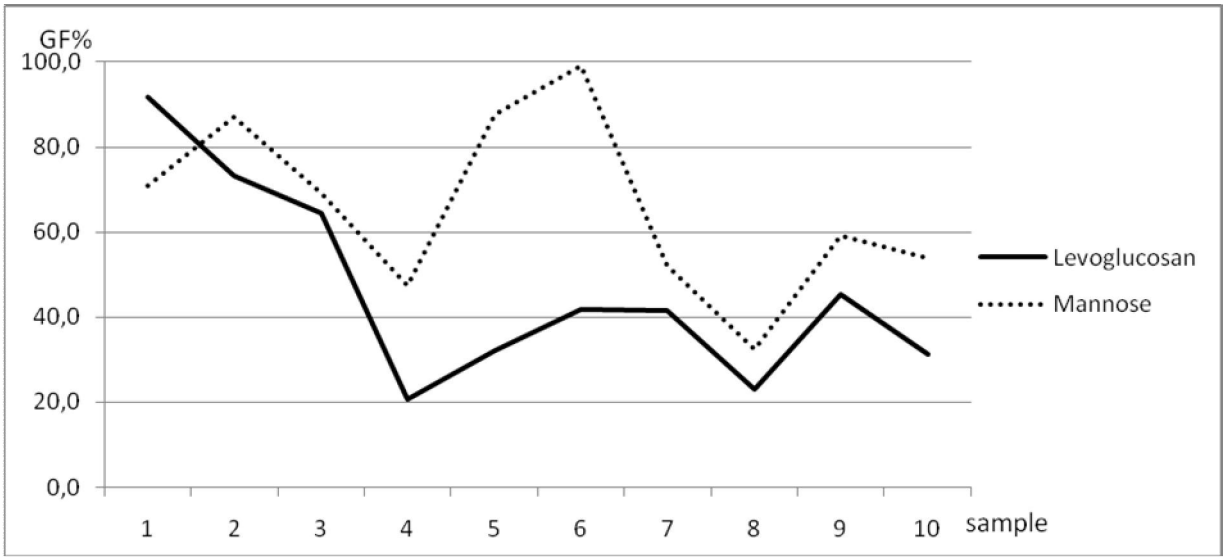

Figure 12. Gas-phase adsorption (in %) of levoglucosan and mannose onto quartz (samples 1-3) and teflon (samples 4-10) filters.

In view of the results (**Paper IV**), both filter materials were concluded to be useful if gas-phase adsorption is taken into account. Quartz is cheaper and suitable for high volume sampling, however, and may often be the better choice.

Table 9. Contribution of gas-phase compounds to the total mass in percent. Q is quartz filter and T is teflon. See text for details.

Compound	18.02-22.02	22.02-26.02	26.02-03.03	03.03-09.03	09.03-16.03	16.03-22.03	22.03-29.03	29.03-07.04	07.04-13.04	13.04-19.04
	50 nm Q	50 nm Q	50 nm Q	50 nm T	50 nm T	50 nm T	40 nm T	40 nm T	40 nm T	30 nm T
Levoglucosan	91.7	73.2	64.4	20.8	32.1	41.8	41.5	22.9	45.5	31.4
L-Mannose	70.8	87.0	69.2	47.5	87.8	99.1	52.1	32.4	59.2	53.8
D-Mannose	-	57.3	74.4	77.2	43.7	49.9	27.1	22.9	29.2	-
Malonic acid	100.0	100.0	93.2	64.1	30.2	22.2	31.4	27.1	48.1	35.2
Maleic acid	-	-	-	-	-	-	-	9.2	23.4	24.4
Malic acid	37.7	83.0	100.0	50.5	100.0	28.4	2.9	3.3	21.8	50.1
Adipic acid	100.0	83.2	100.0	100.0	97.3	69.0	36.9	20.2	42.8	44.7
Azelaic acid	100.0	69.8	80.3	84.6	84.8	13.0	47.0	16.1	38.8	40.8
Tartaric acid	-	6.4	60.0	100.0	100.0	58.2	0.9	5.6	-	-
Octanoic acid	73.7	76.0	61.7	46.0	67.7	33.6	22.5	19.8	20.6	28.5
Palmitic acid	61.4	74.3	81.5	55.4	63.3	46.6	24.8	20.9	24.6	24.0
Vanillic acid	-	-	-	-	-	-	-	-	-	-
cis-Pinonic acid	67.7	87.2	93.3	-	-	-	-	-	-	-
3-Hydroxyglutaric acid	66.8	91.0	76.8	67.1	64.8	44.5	-	-	-	-
Pinic acid	42.6	43.0	52.0	26.3	74.7	34.7	21.9	-	-	-
Benzoic acid	75.5	81.9	100.0	35.8	55.1	33.9	17.7	3.8	18.6	47.6
Mandelic acid	-	-	-	-	-	-	-	-	-	-
Sebacic acid	-	-	-	88.9	84.4	38.0	42.0	60.0	32.0	64.7
Hexanal	55.9	32.3	42.2	25.4	24.6	41.2	98.6	19.2	34.7	24.6
Benzaldehyde	35.5	27.9	28.8	20.9	12.2	21.3	55.3	34.3	22.1	12.2
Heptanal	88.4	32.6	47.6	38.6	47.8	43.1	99.5	38.4	97.2	47.8
Octanal	-	39.8	34.7	35.8	47.4	35.5	66.1	22.6	63.3	47.4
Nonanal	80.6	49.2	34.0	56.9	32.3	28.7	58.1	27.2	75.4	32.3
Pinonaldehyde	54.0	28.8	27.2	19.0	22.8	44.0	96.4	20.3	29.1	22.8
Tridecanal	-	-	-	30.7	29.8	61.5	61.3	39.1	68.0	29.8
β-Caryophyllene aldehyde	47.2	30.4	44.3	20.3	50.4	47.0	71.6	34.4	80.3	50.4
β-Nocaryophyllene aldehyde	-	39.1	42.8	-	43.2	52.9	100.7	15.9	63.7	43.2
EDA	37.8	93.0	30.7	88.8	50.5	84.9	56.5	20.8	50.9	50.5
DEA	34.4	69.0	92.6	76.5	14.7	95.9	54.0	72.2	41.2	14.7
DPA	5.2	16.3	84.5	91.1	52.4	47.5	73.3	57.0	37.4	52.4
pAP	44.8	81.3	100.0	95.4	43.6	72.2	90.1	56.3	95.9	43.6
iPA	87.7	-	6.1	-	44.6	21.8	71.5	10.3	73.4	44.6
iPAn	45.7	69.7	76.5	84.3	41.6	40.9	55.9	43.7	79.2	41.6

5.2 Methodological developments

Aerosol samples potentially contain a great number of compounds covering a wide range of polarities, volatilities and masses. From the analytical point of view they are highly challenging. This section will consider the importance of reference materials for the reliable analysis of aerosol chemical composition and methodological developments.

5.2.1 Synthesis and use of synthesized reference materials

One of the aims of this study was to look for possible oxidation products of β-caryophyllene in boreal forest atmospheric aerosols, since the potential for SOA formation from sesquiterpenes is thought to be higher than that from monoterpenes. One approach is to use characteristic mass spectra obtained from chamber experiment particle analysis. The results of such an investigation can never be more than tentative, however, since oxidation products often have similar mass spectra but substantially different GC retention times. In addition, chamber experiments do not allow reliable quantitative determination, since no authentic standard calibration curves are available. Surrogates might be useful, but the quantitation error would then be high.

Aldehydes from terpenes are present in high quantities in forest aerosols and may play an important role in particle growth [Zhang et al. 1992, Bonn et al. 2003, Liggio et al. 2006a,b, Laaksonen et al. 2008]. In view of this, aldehydes of β-caryophyllene were synthesized (**Paper V**), and two of them, β-caryophyllene aldehyde and β-nocaryophyllene aldehyde, were used for the determination of these compounds in HVS quartz filter samples collected at SMEAR II boreal forest station in 2003. With the aid of an authentic standard, β-nocaryophyllene aldehyde was measured in ambient aerosol samples for the first time. The concentration found with GC-MS was 17.4 ng/m^3. As discovered later, however, owing to overlapping of the aldehydes with other aerosol compounds, the concentration was overestimated. High resolution GC*GC-FID subsequently showed the concentration to be 6 ng/m^3 [Kallio et al. 2009].

The next step in the study of oxidation products was the synthesis of β-caryophyllinic acid. After purification, the amount of acid was not sufficient for structural identification by NMR, but identification could be done by GC-MS and ESI-MS. This standard enabled the reliable

qualitative analysis of β-caryophyllinic acid in PILS samples for the first time. For the quantitation, a surrogate (*cis*-pinonic acid) was used with an estimated error of 50% (**Paper II**). An average concentration of 72 ng/m^3 was found in PILS aerosol samples. The concentration was high compared with the values reported by Jaoui et al. [2007]: in their study the concentrations of β-caryophyllinic acid ranged from just 0.5 to 7 ng/m^3, depending on the time of year. However, because their identification and quantitation were done without an authentic standard and the samples were taken from the forest of North America, the concentrations they report may deviated substantially from ours. Both our and their studies nevertheless indicate that β-caryophyllinic acid contributes to aerosol growth.

The synthesis of 3-hydroxyglutaric acid (HGA) was undertaken to allow us to follow the relations among the oxidation products of α-pinene and so to clarify its atmospheric chemistry. The amount synthesized was sufficient for quantitative determination. Since HGA is one of the oxidation products of pinic acid, it is essential that it be included in standard mixtures for the analysis of biogenic aerosols [Claeys et al. 2007]. When synthesized HGA was included as an authentic standard (**Papers III, IV**), at least two findings emerged. Amounts of HGA in nanometer-size aerosols were smaller than those of pinic acid. Since the relation is usually the opposite in TSP, we can conclude that pinic acid undergoes oxidation already in the particle phase. Also, recent chamber experiments have indicated that pinic acid form in the aerosol phase from precursors [Kanawati et al. 2008], which supports our findings. Furthermore, the oxidation of pinic acid must continue throughout the year, since high concentrations of HGA were present in aerosol samples even in February.

The synthesis of authentic reference compounds has become a necessary step in analytical work, since many of the compounds of interest are not commercially available. Even though sometimes time-consuming, this step cannot be bypassed if analytical results are to be reliable.

6 CONCLUSIONS

Novel instrumental and methodological approaches to sampling of atmospheric aerosols and determination of chemical composition were developed in this research, and the results are summarized and discussed in this thesis.

The sampling of atmospheric aerosols with a particle-into-liquid sampler was modified to allow the collection of samples for off-line gas and liquid chromatographic analysis. It was shown that the amount of organic compounds collected in a two-hour PILS samples was sufficient for conventional analytical techniques. Also, a method involving direct injection of PILS samples to ESI-MS^2 revealed characteristic ions of cleavage of biogenic acid molecules. This was a step towards on-line coupling.

To simplify the sample treatment and allow all steps of the analytical cycle to be performed in a closed system, a novel on-line coupled PILS-SPE-HPLC-MS system was constructed, tested, and optimized. With the on-line coupled system, organic acids in ambient atmospheric aerosols were successfully sampled, treated, and analyzed. The approach can be utilized in future for on-line determinations of other chemical compound groups, since the SAX used in SPE can easily be replaced with other suitable adsorbent material.

As a different approach, DMA-assisted sampling was modified to allow the simultaneous collection of zero (gas-phase) samples. The constructed system enabled the collection of nanometer-sized aerosol particles and, separately, the collection of adsorptive gas-phase compounds for determination of their contribution in the collection of aerosols. It was found that gas-phase adsorption can contribute significantly to the organic carbon mass on aerosol filter and must be taken into account. The setup described for the purpose is easy to construct and should help to correct the overestimation of organic mass due to gas-phase adsorption. Different filter materials for aerosol collection were evaluated. Both teflon and quartz adsorbed the gas-phase compounds, but probably for different reasons. In the case of quartz, adsorption is due to interactions with the filter material surface, but in the case of teflon it is probably due to interactions between gas-phase compounds and the layer of aerosols deposited on the filter surface.

Oxidation products of β-caryophyllene, namely, β-caryophyllene aldehyde, β-nocaryophyllene aldehyde, and β-caryophyllinic acid, were synthesized, purified, and used as reference materials, allowing their reliable verification in ambient aerosol samples for the first time. The concentrations found in HVS, PILS, and DMA size separated samples were relatively high, indicating that these compounds are relevant to aerosol formation or growth or both.

In summary, the novel methodologies presented in this study provide several advantages over conventional approaches. The on-line coupling and automation possible in the described techniques make the monitoring of chemical composition possible even at remote sites. Whereas PILS sampling can be done only for fixed-size aerosols larger than 50 nm, DMA-assisted sampling can be adjusted to collect aerosols of any desired size, with simultaneous correction for the gas-phase adsorption. For the future, longer time series than those used in this study will be needed before we understand adequately the chemistry of aerosol formation and growth.

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